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(56) Documents cited
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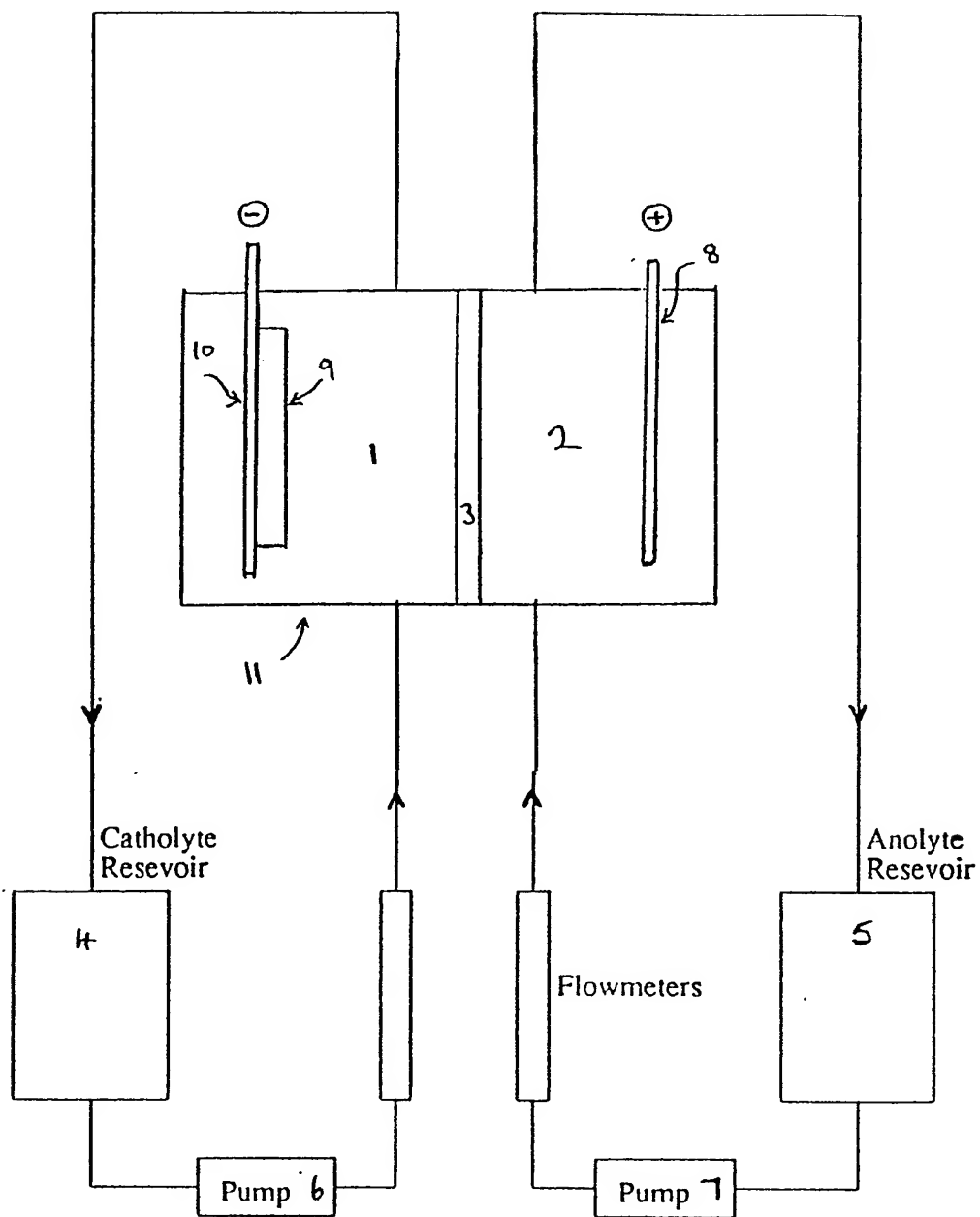
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INT CL⁵ **C02F, C25B**
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(54) **A process for the electrolytic destruction of nitrate in aqueous liquids**

(57) Nitrates in an aqueous liquid are destroyed by circulating through the cathode compartment of an electrolytic cell a liquid which contains the nitrate and in the anode compartment an anolyte, said electrolytic cell comprising a cathode on one side of a cation selective membrane which is permeable to hydrogen ions and an anode on the other side of the membrane, which membrane serves to divide the electrochemical cell into the anode compartment and the cathode compartment, the anolyte comprising a halide free solution comprising an anion which is electrochemically inactive, preferably sulphate ions, e.g. a solution of sulphuric acid or an inorganic sulphate, such as sodium sulphate, and thereafter passing electric current through the electrochemical cell so that nitrate ions in the cathode compartment are reduced to ammonia. The ammonia is separated from the catholyte, dissolved in sulphuric acid and used as the anolyte to oxidize ammonia to nitrogen.

GB 2 267 290 A

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FIG. 1.



A PROCESS FOR THE DESTRUCTION OF
NITRATE IN AQUEOUS LIQUIDS

5 This invention relates to the destruction of
nitrates in aqueous liquids. In many places in
Europe, including the United Kingdom, the use of
fertilisers in agriculture has led to an increase in
the nitrate content of ground water. As a result, the
10 water extracted from some boreholes is now above the
limit of 50mg/litre (50 ppm) which has been set by
European Community legislation. Nitrate-containing
solutions can also arise as a result of various
industrial processes. For example, the treatment of
15 nitrate-containing brackish water by electrodialysis
or reverse osmosis produces a stream in which the
nitrates are concentrated. The washings from plants
using pickle liquors based on nitric acid are another
example. Solutions resulting from the scrubbing of
20 nitric oxides from gas streams will also contain
nitrates.

Removal of nitrate from aqueous liquids by ion
exchange is a favoured technique for treating such
water but regeneration of the resin produces an
25 effluent which is high in nitrate, usually from 3 to 4
g/l and also in chloride. Disposal of this solution
is often expensive or impractical.

In European Patent Application 0 412 175A there
is disclosed a method for removing nitrogen compounds
30 from an aqueous liquid containing nitrogen oxides
and/or nitrates using an electrolytic cell in which
the liquid containing the said nitrogen compound is
electrolysed in the cathode compartment. A
cation-selective membrane separates the cathode
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compartment from the anode compartment and there is used in the anode compartment an anolyte which contains an aqueous solution of an alkali halide, in particular sodium bromide or sodium chloride. While
5 it is essential that the method of EP-A-0 412 175 contains the halide in the anolyte, there is disclosed the use in the anode compartment of a mixture of a solution of hydrogen bromide and sulphuric acid.

The present inventor has carried out research in
10 the destruction of nitrates in aqueous liquids and has surprisingly found that an improved process for destroying nitrates is provided when the anolyte is free of halide ions and comprises an anion which is electrochemically inactive and is preferably sulphate
15 ion but may be phosphate ion (PO_4^{3-}). The reason for this is that several unfavourable reactions occur when halides are introduced into the anode compartment. In the case of chloride, these include the evolution of chlorine, and the formation of
20 chlorate, both of which are toxic. In the presence of ammonia, chlorine may react further to give chloramines, which are lachrymatory. Since the presence of chloride ions in the anolyte should, as a consequence, be avoided, the use of microporous
25 separators, as described in EP-A-0 412 175 is also undesirable. These membranes cannot prevent the transport of chloride from catholyte to anolyte. It is also most unlikely that the desired anodic reaction, i.e. the oxidation of ammonia, could take
30 place to any great extent in the presence of high chloride concentrations, since chlorine evolution will be the favoured reaction. The use of sulphate ions without chloride ions in the anolyte avoids these problems.

35 Accordingly, the present invention provides a
WD8086g

process for destroying nitrates in an aqueous liquid which process comprises circulating through the cathode compartment of an electrolytic cell a liquid which contains the nitrate and in the anode compartment of the electrolytic cell there is circulated an anolyte, wherein said electrolytic cell comprises a cathode on one side of a cation selective membrane which is permeable to hydrogen ions and an anode on the other side of the membrane, which membrane serves to divide the electrochemical cell into the anode compartment and the cathode compartment, and wherein the anolyte comprises a halide free solution comprising an anion which is electrochemically inactive, preferably sulphate ions, e.g. a solution of sulphuric acid or an inorganic sulphate, such as sodium sulphate, and thereafter passing electric current through the electrochemical cell so that nitrate ions in the cathode compartment are reduced to ammonia.

20 Preferably the ammonia produced in the cathode compartment is separated from the catholyte and dissolved into sulphuric acid, thereafter the resulting solution is oxidized to nitrogen in the anode compartment of an electrolytic cell, which is conveniently the same cell in which the ammonia was produced. It is preferred that the cathode of the electrochemical cell is formed of Reticulated Vitreous carbon, which is preferably supported by a carbon backing plate.

30 For ease of operation on a large scale the catholyte and anolyte which are employed in the electrolytic cell are each circulated in a loop to and from the cathode compartment and anode compartment respectively and there is provided a holding tank in

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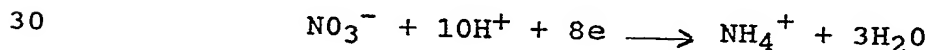
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each loop. It is desirable that the nitrate levels of the cathode compartment are reduced to 50 parts per million or less and that the process is carried out such that a current deficiency of between 50% and 70% is obtained. By prolonged passage of current through the electrochemical cell the nitrate level of the catholyte can be reduced to below 1 ppm.

In a preferred process of this invention ammonia is separated from the catholyte after adjusting the pH to at least 11.5 by contacting outside the cathode compartment said catholyte with a counter flowing stream of inert gas and thereafter dissolving the ammonia gas which has been stripped from the catholyte in a solution of sulphuric acid. The solution containing nitrate ions may also contain chloride ions and this will usually be derived from an ion exchange treatment. After stripping ammonia from the catholyte the solution is alkaline and is preferably neutralised to a pH of 6 to 7.5 and then concentrated by distillation or other means. The solution may then be returned to the ion exchange treatment plant.

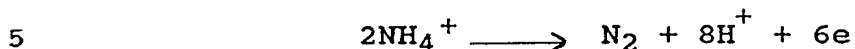
It will be appreciated that the process of this invention operates in three stages:-

(a) Reduction of nitrate to ammonia in the catholyte of the electrochemical cell, according to the equation:



(b) Removal of ammonia from the catholyte as a vapour, and its subsequent dissolution into sulphuric acid.

(c) Oxidation of ammonia to nitrogen in the anode compartment of an electrochemical cell, according to the equation:



The electrochemical cell and the process of this invention will now be described with reference to the accompanying figure.

10 The electrochemical cell (11) which is used in stages (a) and (c) consists of a cathode compartment (1) and an anode compartment (2) divided by a cation selective membrane (3) which is permeable to hydrogen ions and is substantially impermeable to other
15 inorganic ions. Conduction through this membrane is provided by the hydrogen ions. Catholyte and anolyte are circulated from holding tanks (4,5) respectively through the cell compartments using pumps (6,7). The catholyte contains the nitrate to be treated. The
20 anolyte is a solution of sulphuric acid or sodium sulphate. It may also contain the solution of ammonia obtained in stage (b).

The anode (8) may be of a noble metal such as platinum, or platinised titanium. The cathode (9) is
25 carbon. Best results are obtained with a carbon material known as Reticulated Vitreous Carbon (RVC). This is made commercially by pyrolysing a polymer foam. The open porous nature of RVC provides an enhanced surface area for the electrochemical
30 reaction. A block or sheet of RVC is affixed to a non-porous graphite backing plate (10) with nylon screws (not shown). The whole assembly is constructed with materials which are not attacked by the catholyte, which is very corrosive to many materials,
35 such as steel.

WD8086g

A direct current is passed through the cell by attaching electrical leads (not shown) to the cathode backing plate and to the anode. It is advantageous to arrange for the membrane to be close to the RVC, and to the anode, thereby improving the mass transport, and hence the efficiency of the cell.

After the catholyte has been treated in the electrochemical cell, provided it is not strongly buffered, it has a high pH. This facilitates the stripping of ammonia to the vapour phase by boiling, or by contacting the liquid with a gas (such as air) in a suitable apparatus in a manner known per se. The ammonia vapour is easily re-dissolved into sulphuric acid. The resulting solution may then be used as the anolyte in the electrochemical cell, and after converting the nitrate and removing the resultant ammonia, the catholyte may be discarded or neutralised with hydrochloric acid, concentrated by evaporation and reused as regenerant for the ion exchange column.

The sulphuric acid anolyte may be used in a closed loop, with ammonia being dissolved and oxidized electrochemically at appropriate times. The ammonia concentration can be maintained at convenient levels, (it is not necessary to deplete it entirely in each batch). The acid concentration can readily be adjusted by evaporation or dilution, as necessary.

If the overall process is operated as described, the volumes of effluent to be discarded can be minimised. The sulphuric acid can be circulated many times through the anolyte loop by adjusting the water content, and the spent catholyte after neutralisation can be used to regenerate the ion exchange column. This avoids the rejection of large quantities of chloride.

The invention will be illustrated further with reference to the following examples.

1. Reduction of nitrate to ammonia

5 The electrochemical cell of figure 1 was used as follows. The catholyte was 1 litre of solution containing 29.3 gm, NaCl and 4.25 gm, NaNO_3 , i.e. the nitrate ion concentration was 3100 parts per million (ppm). The anolyte was 1 litre of 2.45% sulphuric acid. The anode was a platinised titanium plate with an active area of 75mm x 75mm. The cathode consisted of a block of RVC, facial area 75mm x 75mm x 10mm deep, fixed to a graphite backing plate. The catholyte frame, with entry and exit ports for the flowing solution, fitted closely around the RVC so that any excess of solution to the backing plate was mainly through the pores of the RVC. The membrane was Nafion 417 (a Du Pont product). A current of 3A was passed through the cell and sample analyses gave the data of Table 1.

Table 1

Time (hrs.)	0	1	2	3	4	5	6
25 $[\text{NO}_3^-]$ (ppm)	3100	2221	1523	943	580	134	32
$[\text{NH}_4^+]$ (ppm)	0	190	377	535	673	774	809
pH	9.0	12.0	12.3	12.4	12.4	12.5	12.5

30 The results show that the nitrate concentration may be reduced to below 50 ppm in about 5.75 hours. This corresponds to an overall current efficiency of 64%.

Small amounts of ammonia have been lost, either into the vapour phase, or by transport of the neutral species, NH_3 , across the membrane into the anolyte. The latter is advantageous. Final concentrations of nitrite were <1ppm.

WD8086g

2. Similar experiments were performed using the backing plate alone, i.e. by removing the RVC, or by replacing the RVC with an assembly of carbon chips. Current efficiencies in these cases were 23% and 54%,
5 respectively.

The Nafion membranes are based on perfluorinated ion-exchange polymers. Attached to the fluoropolymer chains are perfluorinated cation exchange sites. The membranes are permeable to cations but one cation is
10 generally more permeable than others. In the case of Nafion 417, hydrogen ions are permeable. The 400 series have sulphonic groups at the active sites. The Nafion membranes are reinforced with a polytetra fluoroethylene support cloth.

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3. Removal of ammonia from the catholyte

The pH of a solution containing 29.3 gm/litre NaCl and 2.14 gm/litre NH_4Cl (i.e. 720 ppm NH_4^+) was adjusted to 12.0. These conditions are equivalent to
20 those of the treated catholyte. The solution was continuously circulated by pumping to the top of a trickle tower containing glass beads, and then returning to a holding container. The temperature was maintained at 50°C. Air was passed upwardly through the tower, in
25 counter flow to the liquid, to strip out the ammonia. The gas stream was then introduced into the bottom of a similar tower through which sulphuric acid solution (2.45%) of the same total volume was descending. The ammonia was re-absorbed into this liquid which was
30 circulated without heating. The ammonia concentrations in each liquid are shown in Table 2.

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WD8086g

Table 2

	Time (hrs.)	0	0.5	1	1.5	2	2.5	3.5
	[NH ₄ ⁺] (ppm)	715	401	229	135	67	36	17
5	(alkali)							
	[NH ₄ ⁺ (ppm)	0	268	449	531	605	633	670
	(acid)							

The results show that ammonia may be transferred from one liquid to the other. The process is accelerated by increasing the temperature of the alkaline-chloride solution side.

4. Oxidation of ammonia in the presence of sulphate

The electrochemical cell was used as previously described. The catholyte was 1.2 litres of NaCl solution (29.3 gm/litre). The anolyte was ammonium sulphate dissolved in 1.2 litres of sodium sulphate solution (35.5 gm/litre) to give a concentration of about 800 ppm NH₄⁺. Both solutions were circulated as before, and a current of 3A was passed. The anolyte rapidly became acidic, and the ammonia concentration decreased as shown in Table 3.

Table 3

25	Time (hrs.)	0	1	2	3	4	6	8
	[NH ₄ ⁺] (ppm)	787	562	422	319	213	141	89
	pH	6.0	2.6	2.2	2.0	1.9	1.7	1.6

The results show that ammonia is oxidized by this method. No nitrate or nitrite was detected in the anolyte.

It is possible to operate a process in accordance

with this invention by transferring the treated
catholyte containing ammonia directly into the anode
compartment to oxidize the ammonia to nitrogen, but for
this to be a useful procedure it is necessary that the
5 electrochemical species present in the solution are
inactive at the anode as well as being inactive at the
cathode. Solutions containing nitrates and sulphate,
which in this connection is an electrochemically
inactive species, can be treated by such procedure. If
10 chloride ions are present in the starting liquid, then
undesirable products, such as chlorate and chloramines
are formed.

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WD8086g

CLAIMS:

1. A process for destroying nitrates in an aqueous liquid which process comprises circulating
5 through the cathode compartment of an electrolytic cell a liquid which contains the nitrate and in the anode compartment of the electrolytic cell there is circulated an anolyte, wherein said electrolytic cell comprises a cathode on one side of a cation selective membrane which
10 is permeable to hydrogen ions and an anode on the other side of the membrane, which membrane serves to divide the electrochemical cell into the anode compartment and the cathode compartment, and wherein the anolyte comprises a halide free solution comprising an anion
15 which is electrochemically inactive, preferably sulphate ions, e.g. a solution of sulphuric acid or an inorganic sulphate, such as sodium sulphate, and thereafter passing electric current through the electrochemical cell so that nitrate ions in the cathode compartment are
20 reduced to ammonia.

2. A process as claimed in claim 1 wherein the ammonia produced in the cathode compartment is separated and dissolved into sulphuric acid and thereafter the
25 resulting solution is oxidized to nitrogen in the anode compartment of an electrolytic cell.

3. A process as claimed in claim 1 or claim 2 wherein the cathode of the electrochemical cell is
30 formed of reticulated vitreous carbon, which is preferably supported by a carbon backing plate.

4. A process as claimed in any one of the preceding claims wherein the catholyte and anolyte
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WD8086g

employed in the electrochemical cell are each circulated in a loop to and from the cathode compartment and anode compartment respectively and there is provided a holding tank in each loop.

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5. A process as claimed in any one of the preceding claims wherein the nitrate level of the cathode compartment is reduced to 50 parts per million or less and the arrangement is such that the current efficiency is obtained of between 50% and 70%.

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6. A process as claimed in claim 5 wherein the nitrate level is reduced to below 1 ppm by prolonged passage of current through the electrochemical cell.

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7. A process as claimed in any one of the preceding claims wherein ammonia is separated from the catholyte after adjusting the pH to at least 11.5 by contacting outside the cathode compartment said catholyte with a counter flowing stream of inert gas and thereafter dissolving the ammonia gas which has been stripped from the catholyte in a solution of sulphuric acid.

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8. A process as claimed in claim 7, wherein resulting solution containing ammonia and sulphate ions is used as anolyte solution in the process as claimed in any one of claims 1 to 6.

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9. A process as claimed in any one of the preceding claims wherein the solution containing nitrate ions also contains chloride ions which is derived from an ion exchange treatment.

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WD8086g

10. A process as claimed in any one of the preceding claims wherein the ammonia solution containing nitrates and electrochemically inactive substances such as sulphate, after the formation of ammonia in the cathode compartment is subsequently treated by using the ammonia-containing catholyte as an anolyte in the said electrochemical cell.

11. A process as claimed in claim 1 and substantially as hereinbefore described with reference to and as illustrated in the figure of the accompanying drawing.

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WD8086g

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

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Relevant Technical fields

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BCFX,BCPA,BPCF,BCPH,BCPL,BCPU

(ii) Int Cl (Edition 5) 002F: C25B

Search Examiner

M J INSLEY

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search

7 OCTOBER 1992

Documents considered relevant following a search in respect of claims 1-11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2211858 A (OLIN) see page 7 lines 21-22 page 11 lines 14-19	1,4 at least
X	GB 2038872 A (ASAHI KASEI KOGYO) see Claim 1	1 at least
X	US 4312722 A (ASAHI KASEI KOGYO) see Claim 1	

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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